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Flame Retardant Mechanism of a Novel Intumescent Flame Retardant Polypropylene

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Abstract

A novel intumescent flame retardant was incorporated into polypropylene to prepare novel intumescent flame retardant composites (PP/IFR) with good flame retardant properties. The flame retardant mechanism was investigated by means of Laser Raman spectroscopy (LRS), X-ray photoelectron spectroscopy (XPS), Thermogravimetric analysis/infrared spectrometry (TGA-IR), Fourier Transform infrared spectroscopy (FTIR) and Energy Dispersive Spectrometer (EDS). It was found that the IFR could decrease the degradation rate of PP; the formed intumescent char was containing unorganized carbon structure and graphitic structure, and consisting of P, N, O and C elements. FTIR analysis showed that the network with P-O-P and P-O-C were formed. EDS analysis results revealed that some P elements were connected to the polyaromatic rings and could form huge connected network.

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Keywords: intumescent flame retardant; mechanism; polypropylene.

1. Introduction

Intumescent flame retardants are the most promising candidate to substitute the halogen-containing flame retardants, which are free of halogen and with relatively high flame retardant efficiency [1-3]. In general, the IFR systems are composed of three components, i.e., an acid source, a carbonization agent (or char forming agent) and a blowing agent. Among these studies, ammonium polyphosphate (APP)/ pentaerythritol (PER)/ melamine (MEL) systems are widely studied [4-8].

However, the traditional IFR additives are susceptible to migration onto the polymer surface during the processing owing to their low molecular weight, and thus decrease the flame retardant efficiency. To solve the shortcomings, high molecular weight, namely oligomeric or polymeric IFRs, have been developed, which provide a good strategy to solve the above problems [9-12].

At the same time, the flame retardant mechanism of APP/PER has been investigated, but it is very complicated and the study of flame retardant mechanism between APP and oligomeric char forming agent was insufficient. In this paper, a novel char-forming agent (CNCA-DA) was used, which is an oligomeric triazine derivative containing aniline, triazine rings and ethylenediamino groups, and the APP and CNCA-DA have been combined together to form a novel IFR system, which was reported in our previous work [13-14]. The aim of this present work is to study the flame retardant mechanism between APP and CNCA-DA by means of Thermogravimetric analysis/infrared spectrometry (TGA-IR), Laser Raman spectroscopy (LRS), X-ray photoelectron spectroscopy (XPS), Energy Dispersive Spectrometer (EDS) and Fourier Transform infrared spectroscopy (FTIR).

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2. Experimental

2.1. Materials

Polypropylene (PP) resin (T30S, melt flow rate: 2-5 g/10min) used in this work was produced by Maomin Petroleum Chemical Company, China. The novel charring-foaming agent (CNCA-DA) was synthesized in our laboratory. Antioxidant 1010 was produced by Ciba Specialty Chemicals, Switzerland. Ammonium polyphosphate (APP) was offered by Shenzhen Anzheng Chemicals Company, China.

2.2. Preparation of PP/IFR composites

PP composites were prepared by mixing pure PP, APP and charring-foaming agent (CNCA-DA) in a two-roll mill via melt blending at 180 °C with a rotor speed of 60 rpm, and the mixing time was 8 min for each sample. Then the composites were pressed on a curing machine for 4 min to produce sheets with various thickness, which were used to produce various dimension sheets in all tests. For comparison, the controlled pure PP sample was also prepared with the same procedures.

2.3. Laser Raman spectroscopy analysis

The laser Raman spectroscopy (LRS) measurements were carried out at room temperature with a Renishaw inVia Raman microspectrometer with excitation by a 514.5 nm helium-neon laser line focused a micrometer spot on the sample surface, and scanning in the 50-4000cm-1 region. To avoid sample heating, the power was kept below 4 MW. Subsequent visual examination of the surface was made systematically in order to check no alteration happened around the focal point.

2.4. X-ray photoelectron spectroscopy (XPS)

The XPS spectra were recorded with a ESCALAB 250 (Thermo Fisher Scientific, UK), using Al Ka excitation radiation (hv=1486.6 eV) and calibrated by assuming the binding energy of carbonaceous carbon to be 284.8eV.

2.5. Thermogravimetric analysis/infrared spectrometry (TGA-IR)

Thermogravimetric analysis/infrared spectrometry (TG-IR) of the samples was performed using the NATZSCH TG209 thermogravimetric analyzer that was interfaced to the Brukar Vactor TM-22 FTIR spectrophotometer. About 30.0 mg of the sample was put in an alumina crucible and heated from ambient to 800℃ at a heating rate of 20℃/min (air atmosphere, flow rate of 35 ml/min).

2.6. Fourier Transform infrared spectroscopy (FTIR)

PP/IFR for FTIR measurements were prepared by making films of the mixture in a hot press and others are using KBr tablets containing char of composites under 450 ^{o}C for different time. The FTIR spectra were obtained using a FTIR spectrophotometer (Nicolet 6700) in the range from 400 to 4000 cm^{-1}.

2.7. Energy Dispersive Spectrometer (EDS)

Energy Dispersive Spectrometer (EDS) analysis were determined on a Philips QUANTA-400 SEM at an accelerating voltage of 20 kV.

3. Results and discussion

3.1. TG-IR analysis

The TG-IR technique that directly gives identification of the volatilized products can significantly contribute to an understanding of thermal degradation mechanisms [15]. Therefore, the volatilized products formed during the thermal degradation of the PP composites were characterized by TG-IR technique under air, as shown in **Fig. 1**, and the assignment of peaks for TG-FTIR was presented in **Table 1**. As can be seen in **Fig. 1(a)**, PP does not have volatilized products before 400 ^{o}C, and then, a large amount of CO, CO_2, H_2O and hydrocarbon were found, which were detected by the FTIR spectra.

However, When APP was incorporated into PP, the behavior of PP/APP composite has changed largely, and the thermal degradation took place at advance, with degradation of NH_3 and H_2O. Meanwhile, the production amounts of CO and CO_2 reduced dramatically, and P-O and P=O absorption peaks appeared at 1285, 1086, 1024 and 886 cm^{-1}, which were contributed to the scissions of polyphosphoric acid [16].

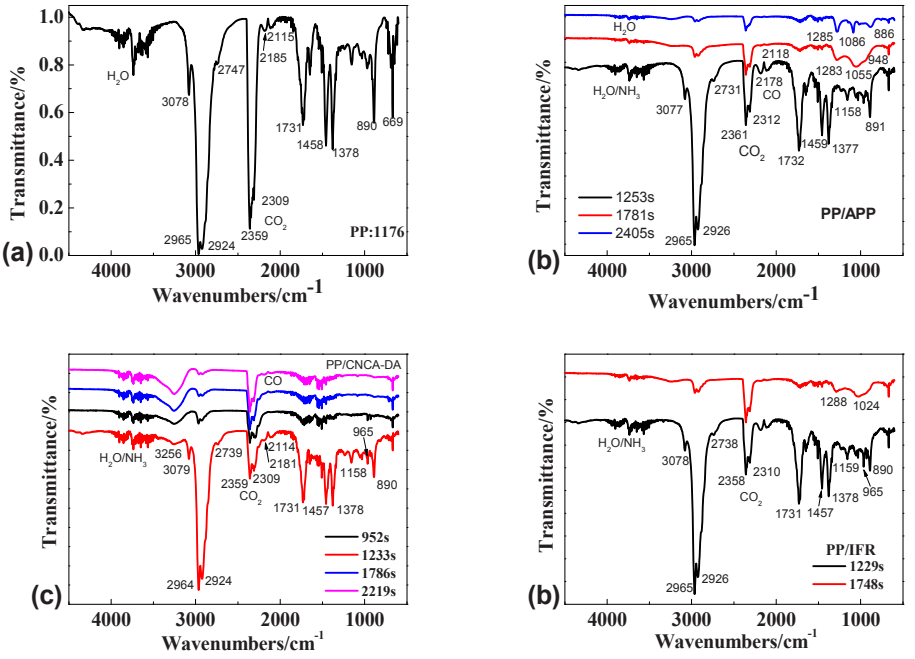

Fig. 1. TG-IR analysis of flame retardant polypropylene composites

（a: PP, b: PP/APP, c: PP/CNCA-DA, d: PP/IFR）

Table 1 Assignment of peaks for TG-FTIR analysis results

2359，2309	CO_2
2185，2115	CO
4000-3200	H_2O or NH_3
3078，2965，2922，1457，1378，890	Saturated and unsaturated C-H
1731	Compound with C=O
669	Aromatic compounds
1285，1086，1024，886	Compound with P-O and P=O

3.2. Chemical composition analysis of final char layer

Raman spectra are usually used to characterize graphitic structure of materials in terms of two characteristic bands: D band (~1360 cm^{-1}, associated with vibration of carbon atoms with dangling bonds in the plane terminations of disordered graphite or glass carbons, representing the unorganized carbon structure) and G band (~1580 cm^{-1}, corresponded to an E2g mode of hexagonal graphite and was related to the vibration of sp2-bonds carbon atoms in graphite layers, showing the graphitic structure) [17-19]. **Fig. 2** presents the Raman spectra of the outer and inner char residue for two samples after combustion. It can be noticed that both of them displayed two visible bands, and these observations provide a positive evidence for the formation of polyaromatic species or graphitic structures [20].

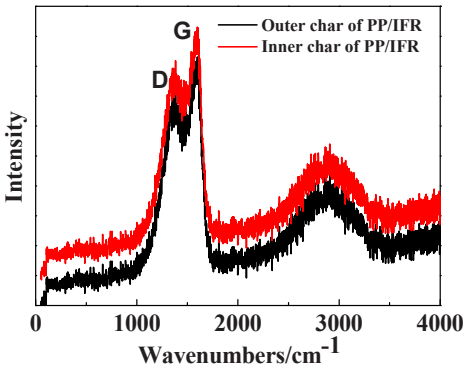

Fig. 2. Raman spectra of char residues after cone test

XPS is an effective measurement to study the surface chemical structure of samples without destruction. The chemical compositions of the outer and inner residual char surface of the PP/IFR composites after cone calorimeter testing were analyzed by XPS. Fig. 3 (a) and (b) are the XPS spectra and relative content of outer and inner residual char surface for the PP/IFR. Peaks at 134.08, 190.90, 284.56, 400.22 and 532.71 eV in Fig. 3(a) can be assigned to P2p, P2s, C1s, N1s and O1s, which mean that both the inner and outer surface of the char consist of P, N, C and O, but the inner char contains higher O/C, P/C and N/C ratio（Fig.3 (b)）. The results can be contributed to the excellent barrier properties of outer char, which can prevent heat and oxygen transferring into the inner materials efficiently. The polyphosphoric acid in the outer surface degraded, and compounds containing P and O were formed and volatilized when combusted.

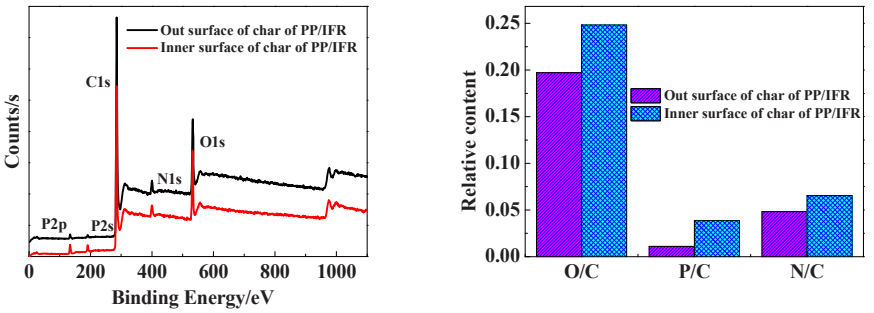

Fig. 3. XPS spectra (a) and relative content (b) of outer and inner chars of PP/IFR

Fig. 4 presents the FTIR spectra of PP/IFR with different heat treatment time at 450 °C, and **Table 2** lists the assignment of the main peaks. It can be found that the relative intensities of C-H absorption peaks decrease as the treatment time increases, but it still remains after PP/IFR was treated for 1 hour. The intensities of O-H or N-H absorption peaks increase as the treatment time increases, which means that APP was degraded to form polyphosphoric acid and NH_3. The absorption peaks of C=C, P-O and P=O are obviously in the FTIR spectra, and its intensity increase with time, which is attributed to the reaction between polyphosphoric acid and hydroxyl compound [21-24]. The results of FTIR studies indicate that polyaromatic structure and interconnecting network comprising P-O-C and P-O-P were formed during the combustion process.

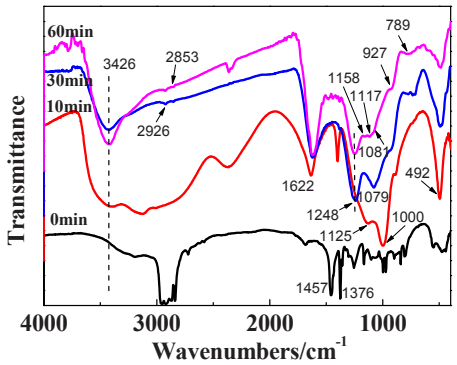

Fig. 4. FTIR spectra of chars for PP/IFR system obtained after heated at 450 oC for different time

Table 2 Assignment of FTIR peaks of chars for PP/IFR system obtained after heated at 450 oC for different time

Peak/cm^{-1}	Assignment	Peak/cm^{-1}	Assignment
3426	OH or NH_4^+	1248	P=O
2926、2853	C-H in hydrocarbon	1158、1000、927、492	P-O in P-O-C
1622	C=C in polyaromatic	1117、1081、1079	P-O in P-O-P

3.3. Chemical composition of char after soaked in water

Fig. 5 gives the XPS spectra of the char before and after soaked in water. It is obviously that the char after soaked in water still comprised P, O, N and C, but their intensity was much lower than those before soaked in water.

The EDS results of the char before and after soaked in water was shown in **Fig. 6**. It was found that the outer and inner char of PP/IFR has similar relative content of P/C, N/C and O/C, which was higher than that of char after soaked in water. Meanwhile, the contents of P and O were 0.50% and 6.21%, which were insoluble in water.

The results from the XPS and EDS studies indicate that some P and O elements were connect directly to the polyaromatic rings or entered into polyaromatic rings.

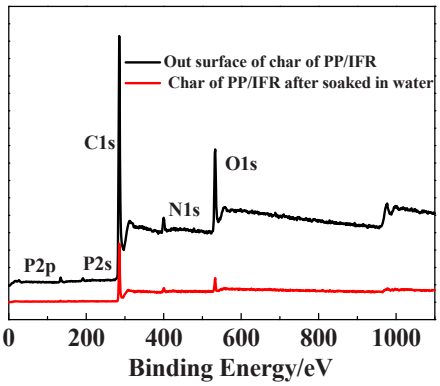

Fig. 5. XPS spectra of char of PP/IFR before or after soaked in water

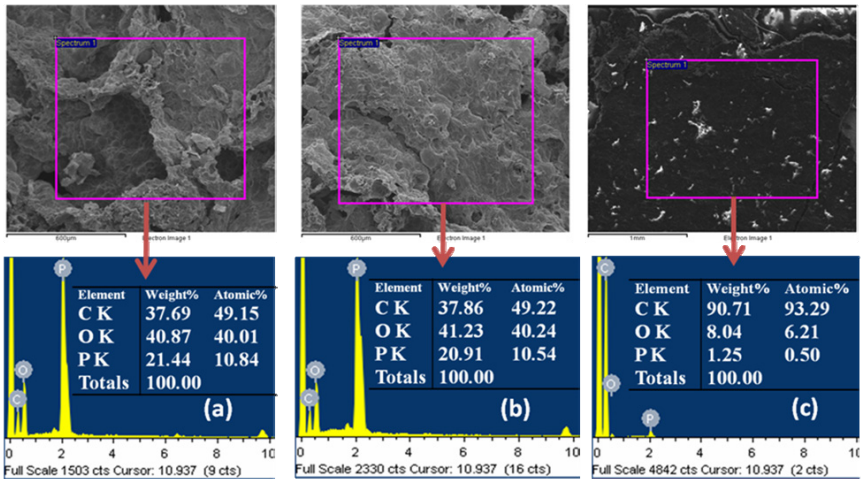

Fig. 6. EDS spectra of char, (a) Outer surface of char；(b) inner surface of char；(c) Residual char after soaked in water

3.4. Flame retardant mechanism

On the basis of the above experimental data from TG-IR, LRS, FTIR, XPS and EDS analysis, the flame retardant mechanism of PP/IFR can be proposed as presented in **Scheme 1**. During burning, the APP component degraded firstly with the release of water and ammonia, and polyphosphoric acid was formed (Reaction 1 in **Scheme 1**). The polyaromatic compounds containing N and P with a large amount of double bond were formed by the catalysis of polyphosphoric acid. At the same time, PP was dehydrogenated and oxidized, with the formation of hydroxyl groups on the backbone and with double bonds from the dehydrogenation, and polyaromatic rings were formed by the connecting reactions of the double bonds (Reaction 2 in **Scheme 1**). Also, ketone and ether were formed by the oxidation of PP (Reaction 3 in **Scheme 1**). The hydroxyl groups from modified PP and polyphosphoric acid were phosphorylated with further dehydration (Reaction 4 and 5 in **Scheme 1**). Crosslinking then occured between polyaromatic rings with hydroxyl groups and the modified APP, and a mixed network would be formed (Reaction 6 in **Scheme 1**). The formation of a small number of such bridges will bring about a stabilization of the APP and a decrease in the volatility of the phosphorus. The consequence was that more P elements will be available for phosphorylation and char formation [25-28].

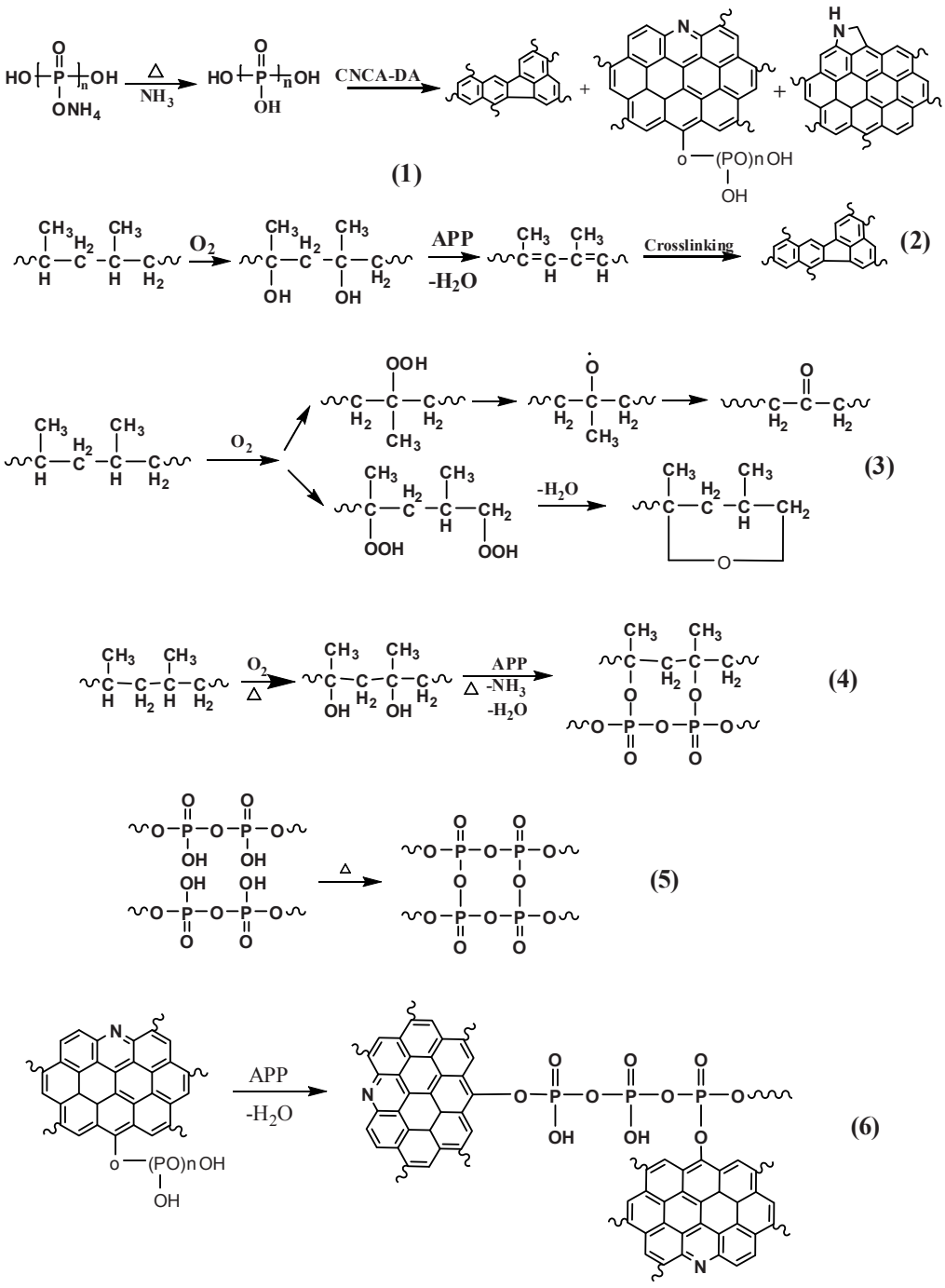

Fig. 7. Sketch map for Flame retardant mechanism of IFR

4. Conclusion

The extended study of the intumescent flame retardant mechanism of the PP/IFR was carried out. The TG-IR results shows that the char formed by APP and CNCA-DA can reduce the further thermal degradation of PP, APP and CNCA-DA. The results of LRS, XPS and EDS studies of the char before and after soaked in water revealed that the burned residue

contains graphitic materials and consists of P, N, C, O. P-O-C and P-O-P connecting network were formed. Both the intumescent charred layers and the graphitic materials formed on the surface of the composites during the combustion process can protect the underlying PP material, and thus improve the flame retardant properties of the composites.

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